Ultrafast Microdynamics of Water and Ice

Edwin J. Heilweil
Optical Technology Division
Physics Laboratory
100 Bureau Drive Stop 8441
National Institute of Standards and Technology
Gaithersburg, MD 20899-8441
Tel: 301-975-2370
Edwin.heilweil@nist.gov

Even the simplest of molecules continues to be elusive. Water can certainly be acknowledged as one of the most important media for supporting various chemical processes and biological functions. Yet, as has been known for years, water exhibits extraordinarily unusual properties such as a high dielectric constant, compressibility, temperature-dependence of the specific heat and viscosity, and most notably, its density. These bulk properties of water and ice have been measured by various physical methods and all are well documented.[1] However, modern spectroscopic techniques are now being brought to bear to decipher the origin of some of water's "anomalous" characteristics. In this Perspective, several current and perhaps controversial experimental and theoretical studies of water and ice using transient infrared spectroscopy and molecular dynamics methods are examined.

Ultrafast mid-infrared (2-10 μm wavelength, 1000-5000 cm^{-1}) spectroscopy has gained in popularity over the past fifteen years because of its sensitivity to molecular vibrational processes and orientation.[2] In principle, whenever an infrared spectrum of a sample can be obtained, detailed information about molecular vibrational energy flow, conformational re-arrangements, chemical reaction intermediates and transitory tertiary structures can be deduced from time-dependent infrared spectra of the system obtained after a perturbation. For example, picosecond (10^{-12} second) or femtosecond (10^{-15} second) ultraviolet laser pulses tuned to a molecular electronic transition of an absorptive, photolabile sample can cause that species to dissociate or react with other molecules. Discretely tunable or broadband infrared (IR) pulses of similar duration are subsequently used to probe the appearance, frequency shift or disappearance of molecular absorptions originating from transiently solvated intermediates, vibrationally "hot" species, and stable products as a function of optical delay time. Analysis of such time-dependent IR spectra allows one to assign the structure of transient species (because of the uniqueness of vibrational spectra to structure) and the temporal evolution of species (by monitoring changes in IR absorption band magnitudes and polarization properties that are concentration and orientation dependent). In this way, detailed microscopic mechanistic information and kinetic rates can be directly obtained for a dynamical system.

These ultrafast infrared technologies are being used to understand the "micro-dynamics" of liquid water and ice. In August 1998, a research group at the FOM Institute for Atomic and Molecular Physics in the Netherlands published the first single-color

femtosecond IR measurements of the OH-stretch vibrational relaxation time (T_1) for water and ice as a function of temperature and state.[3] These results extended earlier spectroscopic and kinetics studies of room temperature water by groups in Germany (see below).[4]

Woutersen, et. al. reported vibrational population decay times (v=1 state) for the OH-stretching mode of HOD molecules dilute in D_2O (see Figure).[3] The temperature dependence of T_1 shows three somewhat unexpected and anomalous features: (1) T_1 is nearly constant for the ice phase (30-270 K), (2) an abrupt increase in T_1 occurs at the 273 K phase transition temperature, and (3) T_1 monotonically increases as the liquid temperature increases to 363 K. Generally accepted theories for the temperature dependence of T_1 consider that for condensed-phase systems, increasing the system temperature leads to an increase in low frequency, energy-accepting mode population.[5] If sufficient coupling exists between a laser-excited vibrational mode and lower frequency "bath" modes, T_1 is predicted to decrease with increasing temperature and the strength of this dependence is related to the system mode frequencies and number of exchanged quanta. Clearly, the new T_1 results for ice and water do not follow this expected behavior. While a few inorganic condensed-phase systems have also been found to display an inverted temperature dependence,[5] Woutersen and colleagues argue that in ice, the strong anharmonically coupled hydrogen-bonded water matrix exists as a double-well potential with similar curvatures in the ground and excited state. This situation leads to a weak occupation number dependence for accepting modes and hence a negligible T_1-dependence on temperature. Also, the density of ice does not change appreciably over the studied temperature range while that of pure water only increases by about 5% from 273 to 363 K. Thus, bulk density or water-water interactions in ice are believed to contribute negligibly to the observed T_1 values.

However, in liquid water, strong variation in the hydrogen-bond strength with temperature occurs (i.e., OH-stretch and hydrogen-bond frequencies in static far, mid-IR and Raman spectra indicate that with increasing liquid temperature, the hydrogen bond strength decreases). In this situation, "if the hydrogen bond forms one of the accepting modes of the vibrational energy, this will lead to an increase of the vibrational lifetime."[3] Similar rationales were applied to early measurements of T_1 in hydrogen-bonded systems such as hydroxyl groups on silica and in micas,[7] mixed acid-base complexes,[8] and in zeolites.[9]

Woutersen, et. al. incorporated the relative change in hydrogen-bond strength with temperature in an analytical hydrogen-bonding model by Staib and Hynes[10] to estimate water OH-stretch T_1 lifetimes. The result of this modeling, normalized to the experimental T_1 value at 325 K, is the dashed curve of the Figure. The fit to the experimental data is excellent, suggesting that the T_1 temperature-dependence could be dominated by changes in average hydrogen-bond strength within the medium. It should be mentioned that molecular dynamics simulations of liquid water as a function of density and temperature, using the best available potentials, obtain an average hydrogen bond lifetime of <10 picoseconds, which is similar to measured vibrational lifetimes.[11]

As one might expect, the story is never so simple. Transient IR investigations of dilute HOD in D_2O at room temperature[4] and up to 343 K[12] using longer IR pulses give ca. 1 ps T_1 lifetimes. Using sophisticated two-color 1-2 ps IR pump-probe hole-burning spectroscopy, one finds that the high frequency OH-stretch absorption (3200-3600 cm^{-1})

is actually composed of three sub-bands (e.g., 45 cm^{-1} wide absorptions from ice-like, dimeric or extended species). These inhomogeneous sub-components exhibit T_1 vibrational lifetimes of 0.8 to 1.5 ps and reorientation times in the 3 to 15 ps range. These observations qualitatively agree with those discussed above, but it is evident that one should probably be careful when using extremely short, spectrally broad IR pulses (e.g., 200 fs, 100 cm^{-1} FWHM[3]) which encompass multiple sub-structures that exist on these short time-scales. One might therefore deduce average T_1 values that reflect the dynamics of all sub-species within the material. In other words, we are slowly learning about the properties of bulk water and ice through its microscopic dynamics, but the intricacies of this important, complex solvent continue to demand further detailed investigation.

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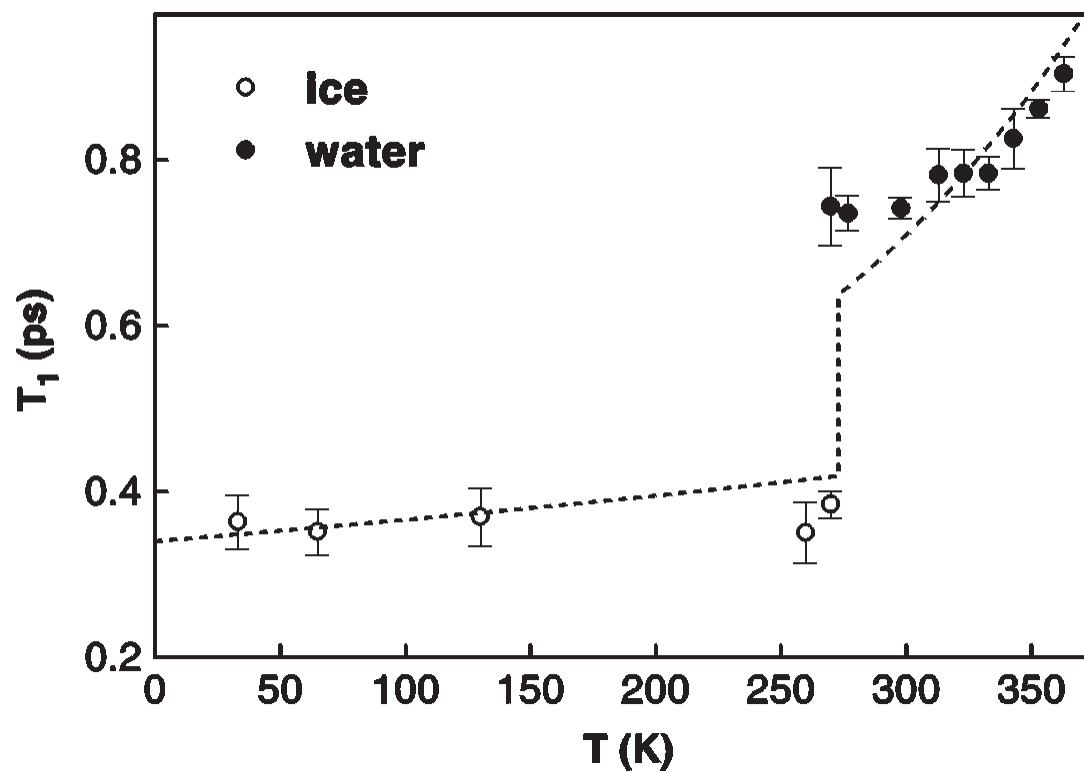
Vibrational lifetime (T_1) of the OH-stretching mode of dilute HOD:D_2O as a function of temperature. The dashed curve is calculated using the hydrogen-bond frequency from the OH-stretch redshift.[10] Printed with permission of the authors.[3]